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Dated 3 June 2004

Patent  
(Rule 1977)06 JUN 03 E812842-3 C03022  
P01/7700 0.00-0312968.1**Request for grant of a patent**

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference

10017

2. Patent application number

(The Patent Office will fill in this part)

0312968.1

5 JUN 2003

3. Full name, address and postcode of the or of each applicant (*underline all surnames*)

BP CHEMICALS LIMITED  
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LONDON  
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UNITED KINGDOM

Patents ADP number (*if you know it*)

4141891002

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

PROCESS FOR THE PRODUCTION OF OLEFINS

5. Name of your agent (*if you have one*)

"Address for service" in the United Kingdom to which all correspondence should be sent  
(*including the postcode*)

PREECE, Michael  
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MIDDLESEX, TW16 7DN  
UNITED KINGDOM

4030177002

Patents ADP number (*if you know it*)6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (*if you know it*) the or each application number

Country

Priority application number  
(*if you know it*)Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
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Continuation sheets of this form

Description	8
Claim(s)	-
Abstract	-
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Priority documents

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination  
(*Patents Form 10/77*)

Any other documents  
(please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature      M. Ree  
PREECE, Michael

Date 5th June 2003

12. Name and daytime telephone number of person to contact in the United Kingdom

(01932) 763201

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## PROCESS FOR THE PRODUCTION OF OLEFINS

The present invention relates to a process for the production of olefins from hydrocarbons in which the hydrocarbons are treated to autothermal cracking.

Autothermal cracking is a new route to olefins in which the hydrocarbon feed is mixed with oxygen and passed over an autothermal cracking catalyst. The autothermal cracking catalyst is capable of supporting combustion beyond the fuel rich limit of flammability. Combustion is initiated on the catalyst surface and the heat required to raise the reactants to the process temperature and to carry out the endothermic cracking process is generated in situ. Generally the hydrocarbon feed and the oxygen is passed over a supported catalyst to produce the olefin product. Typically, the catalyst 5 comprises at least one platinum group metal, for example, platinum. The autothermal cracking process is described in EP 332289B; EP-529793B; EP-A-0709446 and WO 10 00/14035.

The catalyst supports are usually non metallic and are typically ceramic materials, usually in the form of foams, pellets, beads, spheres, tablets and/or extrudates. 15 However whilst generally being chemically inert non metallic supports can often be thermally unstable which results in support cracking. The catalyst support may also be metallic. Due to their malleable nature metallic supports do not exhibit support cracking but are often incapable of withstanding excessive front face temperatures that are produced in the autothermal reactor which leads to oxidation and corrosion. 20 Consequently there is a need to provide an improved support that is both chemically inert and thermally stable.

It has now been found that the autothermal cracking process can be improved by

employing a catalyst with a modified metallic support.

Accordingly, the present invention provides a catalyst capable of supporting combustion beyond the fuel rich limit of flammability comprising a catalytic component and a metallic support wherein the support is at least partially provided with a non metallic coating.

The present invention also provides a process for the production of an olefin, said process comprising passing a mixture of a hydrocarbon and an oxygen-containing gas over a catalyst as herein described above to produce said olefin.

Preferably, the catalyst component comprises a Group VIIIIB metal. Suitable Group VIIIIB metals include platinum, palladium, ruthenium, rhodium, osmium and iridium. Preferably, the Group VIIIIB metal is selected from rhodium, platinum, palladium or mixtures thereof. Especially preferred are platinum, palladium or mixtures thereof. Typical Group VIIIIB metal loadings range from 0.01 to 50 wt %, preferably, from 0.01 to 20 wt %, and more preferably, from 0.01 to 10 wt %, for example 1-5 wt%, such as 3-5 wt%. Suitably, the first catalyst bed comprises platinum or palladium, especially platinum.

Preferably the catalyst component may be a promoted catalyst component such as a promoted Group VIIIIB metal catalyst. The promoter may be selected from the elements of Groups IIIA, IVA and VA of the Periodic Table and mixtures thereof.

Alternatively, the promoter may be a transition metal; the transition metal being a different metal to the catalyst component, such as the Group VIIIIB metal(s) employed as the catalytic component.

The promoter may also be selected from any of the lanthanide metal oxides.

Preferred Group IIIA metals include Al, Ga, In and Tl. Of these, Ga and In are preferred. Preferred Group IVA metals include Ge, Sn and Pb. Of these, Ge and Sn are preferred, especially Sn. The preferred Group VA metal is Sb. The atomic ratio of Group VIIIIB metal to the Group IIIA, IVA or VA metal may be 1 : 0.1 - 50.0, preferably, 1: 0.1 - 12.0, such as 1 : 0.3 - 5.

Suitable transition metal promoters may be selected from any one or more of Groups IB to VIIIB of the Periodic Table. In particular, transition metals selected from Groups IB, IIB, VIB, VIIB and VIIIB of the Periodic Table are preferred. Examples of such transition metal promoters include V, Ni, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co,

Rh, Ir, Ni, Pt, Cu, Ag, Au, Zn, Cd and Hg. Preferred transition metal promoters are Mo, Rh, Ru, Ir, Pt, Cu and Zn, especially Cu. The atomic ratio of the Group VIIIB metal to the transition metal promoter may be 1: 0.1 - 50.0, preferably, 1:0.1 - 12.0.

Specific examples of promoted Group VIIIB metals for use as the promoted catalyst component include Pt/Ga, Pt/In, Pt/Sn, Pt/Ge, Pt/Cu, Pd/Sn, Pd/Ge, Pd/Cu and Rh/Sn. Where the Group VIIIB metal is Rh, Pt or Pd, the Rh, Pt or Pd may comprise between 0.01 and 5.0 wt %, preferably, between 0.01 and 3.0 wt %, and more preferably, between 0.5 and 3.0 wt % of the total weight of the catalyst. The atomic ratio of Rh, Pt or Pd to the Group IIIA, IVA, VA or transition metal promoter may be 1 : 0.1 - 50.0, preferably, 1: 0.1 - 12.0. For example, atomic ratios of Rh, Pt or Pd to Sn may be 1: 0.1 to 50, preferably, 1: 0.1 - 12.0, more preferably, 1: 0.2 - 5.0 and most preferably, 1: 0.3 - 5.0. Atomic ratios of Pt or Pd to Ge may be 1: 0.1 to 50, preferably, 1: 0.1 - 12.0, and more preferably, 1: 0.5 - 8.0. Atomic ratios of Pt or Pd to Cu may be 1: 0.1 - 3.0, preferably, 1: 0.2 - 2.0, and more preferably, 1: 0.3 - 0.5.

For the avoidance of doubt, the catalyst component and the promoter may be present in any form, for example, as a metal, or in the form of a metal compound, such as an oxide.

The metallic support may be selected from any suitable metal. Suitable metals may include steel (mild and high carbon), stainless steel, hastaloy, Ni-Chrome, Inconel, Monel, nickel, copper, iron, platinum, noble metals and their alloys, cobalt, FeCrAlY, or any alloy containing Y, Cr, Fe, Ni and Al e.g Kanthal, Incoloy MA956 or CoCrAlY.

Preferably the metal has a melting point of greater than 1200°C and most preferably the metal is selected from FeCrAlY, CoCrAlY, Ni-Chrome, Inconel and monel. Wherein the metal is an alloy advantageously the alloy does not comprise molybdenum, tungsten, rhenium and/or osmium.

The support type could be selected from anyone of the following; foams, channeled monoliths, mats, fibres, gauzes, pellets, beads, spheres, tablets and/or extrudates. The support is preferably a foam.

The structural dimensions of the support type may also vary.

Wherein the support is in the form of a foam, the foams usually have a pore size in the range of 10ppi to 100ppi and preferably between 30 to 45ppi. These foams typically have a density of from between 60% to 99% of theoretical density of a fully

dense material.

Wherein the support material is in the form of a monolith the monolith is provided with channels. These channels may be of any suitable shape the preferred ones being square, rectangular, triangular, hexagonal and circular. Typically the channels do 5 not pass directly through the monolith and usually the channels provide a complex passageway through the monolith. Usually the monolith has between 2000cpi (cells per inch) to 5cpi and preferably between 1000cpi to 10cpi.

Wherein the support is in the form of a gauze the wire thickness is usually from 0.1mm to 3mm with a mesh size of from 250 wires per inch to 4 wires per inch.

10 Wherein the support is in the form of pellets, beads, spheres, tablets and/or extrudates the external dimensions are usually within the range of between 0.1mm-50mm and advantageously within the range of 0.5mm to 20mm.

Wherein the support is in the form of a foam, monolith or gauze the support 15 preferably usually preferably comprises a series of blocks or layers that tessellate together to leave no gaps. Preferably these blocks or layers are tiled within the reactor in different directions and most preferably in a manner such that tiles of a layer either above or below do not exactly overlap with any neighbouring layer.

The non metallic coating is usually a ceramic material which may be any oxide 20 or combination of oxides that is stable at high temperatures of, for example, between 600°C and 1200°C. The ceramic material preferably has a low thermal expansion coefficient, and is resistant to phase separation at high temperatures.

Suitable ceramic materials include alumina, silica-alumina, a combination of 25 alumina and mullite, lithium aluminium silicate, cordierite, silicon carbide, zirconia toughened alumina, partially stabilized zirconia, fully stabilized zirconia, spinel, chromia, titania, aluminium titanate, or any combination of the above.

The non-metallic coating may be loaded onto the metallic support by any method known in the art. In particular the non-metallic coating may be loaded onto the support by any one of the following methods; aluminizing, chemical vapour deposition, sputter coating and washcoating.

30 Wherein the non metallic coating is alumina, aluminizing deposits aluminium metal onto the surface layer of the metallic support. Usually aluminizing comprises heating the metallic support in a crucible with aluminium powder. The aluminium

deposited upon the surface of the metallic support is then oxidized to form alumina.

Wherein chemical vapour deposition is used to provide a non-metallic coating on the metallic support this usually involves the thermal decomposition of a volatile material onto the surface of a heated metallic support.

5 Wherein sputter coating is used to provide a non-metallic coating on the metallic support the metallic support is spray coated with a fine particulate material which typically contains some sort of binder such that it sticks to the surface of the support. Sputter coating may be performed by arc or laser ablation.

10 In a preferred embodiment of the invention washcoating is used to provide a non-metallic coating on the metallic support. Washcoating involves providing a slurry of the non metallic coating which is then poured through/over the metallic support. Typically the slurry of the non metallic coating is a ceramic coating and is preferably an alumina colloidal suspension with a carefully defined viscosity and particle size.

15 Wherein aluminizing is used the thickness of the non metallic coating is usually between 10-200 $\mu\text{m}$  and preferably between 50-100 $\mu\text{m}$ .

Wherein sputter coating is employed the thickness of the non metallic coating is usually between 10 $\mu\text{m}$ -2mm and preferably between 0.1-1mm..

Usually the % weight of coating relative to the weight of support is less than 5wt%, and preferably less than 3wt%.

20 Preferably substantially all of the metallic support is coated with the non metallic coating.

The catalyst component employed in the present invention may be loaded onto the coated metal support by any method known in the art. For example, gel methods and wet-impregnation techniques may be employed. Typically, the support is impregnated 25 with one or more solutions comprising the metals, dried and then calcined in air. The support may be impregnated in one or more steps. Preferably, multiple impregnation steps are employed. The support is preferably dried and calcined between each impregnation, and then subjected to a final calcination, preferably, in air. The calcined support may then be reduced, for example, by heat treatment in a hydrogen atmosphere.

30 Preferably when the catalyst is positioned within the autothermal cracking reactor a non catalytic resistance zone is located upstream of the catalyst. The resistance zone usually comprises a network of capillaries or channels and most preferably the

resistance zone comprises a porous material and advantageously the porous material is a non metal e.g. a ceramic material. Suitable ceramic materials include lithium aluminium silicate (LAS), alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), yttria stabilised zirconia, alumina titanate, niascon, and calcium zirconyl phosphate. A preferred porous material is  
5 gamma alumina. The porous material may be in the form of spheres, other granular shapes or ceramic foams. Typically the resistance zone has between 10-60 pores per square inch, preferably between 20-50 pores per square inch and most preferably between 30-45 pores per square inch.

The process of the present invention may be used to convert both liquid and  
10 gaseous hydrocarbons into olefins. Suitable liquid hydrocarbons include naphtha, gas oils, vacuum gas oils and mixtures thereof. Preferably, however, gaseous hydrocarbons such as methane, ethane, propane, butane and mixtures thereof are employed. Suitably, the hydrocarbon is a paraffin-containing feed comprising hydrocarbons having at least two carbon atoms.

15 The hydrocarbon feed is mixed with any suitable oxygen-containing gas. Suitably, the oxygen-containing gas is molecular oxygen, air, and/or mixtures thereof. The oxygen-containing gas may be mixed with an inert gas such as nitrogen or argon.

Additional feed components may be included, if so desired. Suitably, hydrogen, carbon monoxide, carbon dioxide or steam may be co-fed into the reactant stream.

20 Any molar ratio of hydrocarbon to oxygen-containing gas is suitable provided the desired olefin is produced in the process of the present invention. The preferred stoichiometric ratio of hydrocarbon to oxygen-containing gas is 5 to 16, preferably, 5 to 13.5 times, preferably, 6 to 10 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas required for complete combustion of the hydrocarbon to carbon dioxide  
25 and water.

The hydrocarbon is passed over the catalyst at a gas hourly space velocity of greater than 10,000 h<sup>-1</sup>, preferably above 20,000 h<sup>-1</sup> and most preferably, greater than 100,000 h<sup>-1</sup>. It will be understood, however, that the optimum gas hourly space velocity will depend upon the pressure and nature of the feed composition.

30 Preferably, hydrogen is co-fed with the hydrocarbon and oxygen-containing gas into the reaction zone. The molar ratio of hydrogen to oxygen-containing gas can vary over any operable range provided that the desired olefin product is produced. Suitably,

the molar ratio of hydrogen to oxygen-containing gas is in the range 0.2 to 4, preferably, in the range 1 to 3.

Hydrogen co-feeds are advantageous because, in the presence of the catalyst, the hydrogen combusts preferentially relative to the hydrocarbon, thereby increasing the  
5 olefin selectivity of the overall process.

Preferably, the reactant mixture of hydrocarbon and oxygen-containing gas (and optionally hydrogen co-feed) is preheated prior to contact with the catalyst. Generally, the reactant mixture is preheated to temperatures below the autoignition temperature of the reactant mixture.

10 Advantageously, a heat exchanger may be employed to preheat the reactant mixture prior to contact with the catalyst. The use of a heat exchanger may allow the reactant mixture to be heated to high preheat temperatures such as temperatures at or above the autoignition temperature of the reactant mixture. The use of high pre-heat temperatures is beneficial in that less oxygen reactant is required which leads to  
15 economic savings. Additionally, the use of high preheat temperatures can result in improved selectivity to olefin product. It has also been found that the use of high preheat temperatures enhances the stability of the reaction within the catalyst thereby leading to higher sustainable superficial feed velocities.

The process of the present invention may suitably be carried out at a catalyst exit  
20 temperature in the range 600°C to 1200°C, preferably, in the range 850°C to 1050°C and, most preferably, in the range 900°C to 1000°C.

The process of the present invention is usually operated at a pressure of greater than 0.5barg. Preferably the autothermal cracking process is operated at a pressure of between 0.5-40barg and advantageously between 10-30barg e.g. 15-25barg.

25 The reaction products are preferably quenched as they emerge from the reaction chamber to avoid further reactions taking place. Usually the product stream is cooled to between 750-600°C within less than 100milliseconds of formation, preferably within 50milliseconds of formation and most preferably within 20milliseconds of formation e.g. within 10milliseconds of formation.

30 Wherein the autothermal cracking process is operated at a pressure of 5-20 barg usually the products are quenched and the temperature cooled to between 750-600°C within 20milliseconds of formation. Advantageously wherein the autothermal cracking

process is operated at a pressure of greater than 20barg the products are quenched and the temperature cooled to between 750-600°C within 10milliseconds of formation.

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